

A Density Functional Approach to Wetting Behaviors of Ternary Water + Oil + Amphiphile Mixtures

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In this study, a microscopic Helmholtz free energy model based on perturbation theory was used to explore the wetting behavior of ternary water-oil-amphiphile mixtures. The three components were modeled as equal-sized hard sphere molecules. The statistical associating fluid theory of Wertheim was used to simulate the associating interaction between water and amphiphile molecules. The density functional theory was applied to calculate the density profile across the interface and the interfacial tension between coexisting phases. The wetting behavior at interfaces was determined according to the relationship between interfacial tensions. The proposed Helmholtz free energy model can successfully mimic the phase behavior of the ternary mixture water-oil-amphiphile. It is well understood that there exist both upper and lower critical endpoints in the ternary mixture water-oil-amphiphile at three-liquid-phase-coexisting region. The occurrence of wetting transitions in such system brought to its critical endpoint was systematically explored. One can observe for certain systems a sequence of wetting transitions for the middle amphiphile-rich phase at the interface separating the oil-rich and aqueous phases: dewetting \rightarrow partial-wetting \rightarrow dewetting along with increasing temperature. With tuning the hydrophobicity of the amphiphile, one can even observe another sequence of wetting transitions: dewetting \rightarrow partial-wetting \rightarrow complete-wetting along with increasing temperature. The effect of the association strength on wetting behavior was also examined. The predictions are compared to experimental observations on wetting behaviors of ternary water-alkane-CiEj mixtures, where CiEj is the abbreviation of a nonionic surfactant polyoxyethylene alcohol $\text{CiH}_{2i-1}(\text{OCH}_2\text{CH}_2)_j\text{OH}$. The order of wetting transitions is also discussed.